

SOME NEW DERIVATIVES
OF THE
MONO NITRO
ORTHO PHTHALIC ACIDS.

By
LEOPOLD BOROSCHEK, B.S., A.M.

A DISSERTATION
SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE FACULTY OF PURE SCIENCE, COLUMBIA UNIVERSITY.

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L. B.

ORGANIC CHEMICAL LABORATORY,
HAVEMEYER HALL, COLUMBIA UNIVERSITY,
October, 1901.



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NOTICE.—All references to page numbers occurring in the text in the body of the work should have two added—7 to 9, 8 to 10, etc.

INTRODUCTION.

I. There are but two mono-nitro substitution products of orthophthalic acid theoretically possible, both of which are known.

In 1841 Marignac,¹ by heating naphthalene with nitric acid, obtained an acid which he named "nitronapthalinsäure." In 1842 Laurent² obtained an acid by treating naphthalene in the same way, which he called "nitrophthalinsäure." This acid, now known as 3 nitro-o-phthalic acid, was next prepared by Müller,³ in 1863, by boiling phthalic acid with concentrated nitric acid. He observed that the acid was always accompanied by a second, noncrystallizable acid.

In 1869 Faust⁴ nitrated phthalic acid with a mixture of nitric and sulphuric acids and obtained 3 nitro-o-phthalic acid. It was not until 1877 that iso- or 4 nitro-o-phthalic acid was isolated and studied by Miller.⁵ He obtained it together with the 3 nitro-o-phthalic acid by treating orthophthalic acid with a mixture of nitric and sulphuric acids.

In 1880 Beilstein and Kurbatow⁶ made the 3 nitro-o-phthalic acid by oxidizing α -nitronaphthalene with a mixture of chromic acid anhydride and acetic acid. In 1885 Hoenig⁷ obtained the 4 nitro-o-phthalic acid by heating paranitrophthalide with dilute nitric acid in a sealed tube.

The following work records the experiments made by the writer in preparing derivatives of the mononitro-o-phthalic acids, similar to some of those, that have already been prepared from the unsubstituted orthophthalic acid.

In order to carry on this work, which required large amounts of the absolutely pure acids, a careful study of the different methods

¹ Ann. Chemie (Liebig), 38, 7.

² Ann. Chemie (Liebig), 41, 110.

³ Zeit. für Chemie, 1863, 257.

⁴ Zeit. für Chemie, 1869, 108.

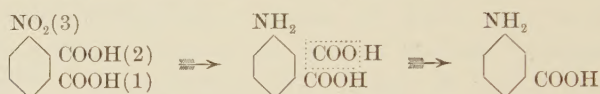
⁵ Ber. d. Chem. Ges., 10, 709.

⁶ Ann. Chemie (Liebig), 202, 217.

⁷ Ber. d. Chem. Ges., 18, 3448.

of preparation and general properties of the acids was found to be necessary.

These acids are stronger acids than phthalic acid, owing to the strongly negative nitro group which they contain. It was found by Faust¹ and also by Miller² that when 3 nitro-o-phthalic acid was treated with tin and hydrochloric acid, a double salt of tin and amidophthalic acid formed, which broke up into carbon dioxide and meta-amidobenzoic acid, when the tin was precipitated with hydrogen sulphide, the reaction being as follows:



Miller³ found that when 4 nitro-o-phthalic acid was reduced, it was also converted into meta-amidobenzoic acid according to the following reaction:



Since the reduction of the nitro to the amido group in 3 nitro-o-phthalic acid causes the loss of that carboxyl group upon which the nitro group exerts its greatest influence, *i. e.*, the adjacent and therefore, the more strongly acid carboxyl, and since by a similar reduction of 4 nitro-o-phthalic acid, the carboxyl in the para position to the nitro group was removed, it is very probable that this carboxyl group in 4 nitro-o-phthalic acid, and not the carboxyl meta to the nitro group is the more strongly acid group.

This reaction is of importance in at least furnishing some foundation for assuming the probable constitutional formulas for the acid salts of the mono nitro-o-phthalic acids, and also for the nitro phthalamic acids.

It has been found by Miller⁴ and also by Wegscheider and Lipschitz,⁵ that in the main Meyer's rule⁶ applies to the esterifi-

¹ Ann. Chemie (Liebig), 160, 61.

² Ber. d. Chem. Ges., 11, 993.

³ Ber. d. Chem. Ges., 11, 992.

⁴ Ann. Chemie (Liebig), 208, 234 and 243.

⁵ Monats. f. Chemie (Wien), 21, 787.

⁶ Ber. d. Chem. Ges., 27, 3150.

cation of these acids. Thus while the 3 nitro-o-phthalic acid forms an acid ester readily and a neutral ester with great difficulty, the neutral ester of 4 nitro-o-phthalic acid can readily be obtained.

These acids undergo decomposition when heated with a strong caustic alkaline solution, owing to the presence of the nitro group. The writer has also found that in some cases the nitro group can be directly replaced by halogen.

II. EXPERIMENTAL PART FOR 3 NITRO-ORTHO-PHTHALIC ACID.

PREPARATION OF THE ACID.

Several methods were tried by the writer for obtaining the pure 3 nitro-o-phthalic acid in fairly large amounts. Of these, the method of Beilstein and Kurbatow¹ was first tried. It consists in oxidizing an acetic acid solution of α nitronaphthalene with chromic acid anhydride.

The writer has found this method to be unsatisfactory for several reasons. In the first place, owing to the violence with which the reaction proceeds, not more than 20 gms. of α nitronaphthalene can be treated at one time; secondly, only 75 per cent. of the nitronaphthalene was attacked by the oxidizing agent, the rest can be recovered unchanged. Then the method is long and tedious and the yield of acid was only 20 per cent. of the theoretical. Finally the 3 nitro-o-phthalic acid obtained through this method did not crystallize well, and was colored pink and melted at 212° (uncorrected).

The method published by Miller² was then tried and yielded fairly satisfactory results. In an attempt to improve upon this method the following modifications of the original method were tried.

I. Direct nitration of orthophthalic acid.

(a) The 3 nitro-o-phthalic acid was separated by crystallizing the nitrated product from water.

(b) The nitrated product was renitrated and the acid separated as in *a*.

¹ Ann. Chemie (Liebig), 202, 217.

² Ann. Chemie (Liebig), 208, 224.

II. Direct nitration of phthalic anhydride.

(a) The 3 nitro-o-phthalic acid was obtained from the nitrated product as in I. (a).

(b) The nitrated product was renitrated and the acid separated as in I. (a).

I. NITRATION OF ORTHOPHTHALIC ACID.

To 100 gms. of orthophthalic acid contained in a $1\frac{1}{2}$ liter flask was added 150 gms. of concentrated sulphuric acid and then 150 gms. of fuming nitric acid. The mixture was heated on the water-bath. After heating one-half an hour, the phthalic acid dissolved, forming a clear amber-colored solution, copious fumes of oxides of nitrogen being given off. After one and one-half hours had elapsed, crystals of nitrophthalic acid began to precipitate. Finally after two hours of heating, the mixture in the flask was almost solid.

When cold 240 cc. of water was added, and the mixture allowed to stand in a cool place over night. The precipitate, consisting of a mixture of the 3 and 4 nitro-o-phthalic acids, together with small amounts of phthalic and picric acids, was filtered off through a suction funnel fitted with a linen filter, and freed as far as possible from the strongly acid mother liquor.

(a) The precipitate obtained above, was dissolved in hot water and the solution concentrated until the 3 nitro-o-phthalic acid began to crystallize from the hot solution. This solution was then allowed to cool slowly and to stand from four to five hours. Nearly all the 3 nitro-o-phthalic acid separates as a thick adherent crust consisting of small, hard, pale yellow transparent crystals.

The crystals were freed from the thick yellow mother liquor, containing besides all the 4 nitro-o-phthalic acid and impurities also a little of the 3 nitro acid. The acid, on being recrystallized from water, was absolutely pure. It melted at 217° . The yield was 28 per cent. of the theoretical or 36 per cent. of the weight of the phthalic acid used.

(b) The precipitate obtained from the first nitration was renitrated, using the same amounts of nitric and sulphuric acids, and keeping the conditions exactly the same, as for the first nitration.

During this nitration only a small portion of the solid dissolved in the hot acid. The yield of pure 3 nitro-o-phthalic acid by this method was 31.5 per cent. of the theory or 40 per cent. of the weight of the phthalic acid originally employed.

II. NITRATION OF PHTHALIC ANHYDRIDE.

100 gms. of phthalic anhydride was treated with a mixture of 150 gms. of concentrated sulphuric and 150 gms. of fuming nitric acids and the nitration was carried on in a similar manner to the nitration of phthalic acid. After 20 minutes of heating, the phthalic anhydride had completely dissolved in the acid mixture and within one hour, the nitro-o-phthalic acid began to precipitate. A few minutes later the contents of the flask was nearly solid, but the heating was continued for one and one-half hours longer.

(a) The yield of pure 3 nitro-o-phthalic acid obtained by crystallizing the nitration product from water was 23 per cent. of the theory or 32.6 per cent. of the weight of phthalic anhydride employed. The yield would have probably been greater if the calculated amount of water necessary to convert the phthalic anhydride to phthalic acid, had been added as soon as the precipitation of the nitrophthalic acids began, during the nitration.

(b) The nitrated product obtained above was renitrated under the same conditions. The yield of pure 3 nitro-o-phthalic acid was 36.4 per cent. of the theoretical or 52 per cent. of the weight of the phthalic anhydride originally used.

As the result of this investigation the writer recommends as the best methods for obtaining the 3 nitro-o-phthalic acid, the method in which a single nitration of phthalic acid was employed, and since phthalic anhydride is cheaper and more readily obtainable, also the method in which a double nitration of phthalic anhydride was used.

PROPERTIES OF 3 NITRO-O-PHTHALIC ACID.

The 3 nitro-o-phthalic acid is a fairly strong acid, forming acid and neutral salts readily with caustic alkalis, but only a neutral ammonium salt in concentrated solutions. With aniline and other amines it forms acid salts only.

SOLUBILITY OF 3 NITRO-O-PHTHALIC ACID.

Solvent.	Cold.	Hot.	Crystals on Cooling.
1. Water.	Difficultly.	Easily.	Good.
2. Petroleum ether.	Insoluble.	Insoluble.	—
3. Benzine.	"	"	—
4. Chloroform.	"	"	—
5. Carbon tetrachloride.	"	"	—
6. Methyl alcohol.	Moderately.	Easily.	Good.
7. Ethyl alcohol (absol.)	"	"	"
8. Isoamyl alcohol.	Sparingly.	Moderately.	—
9. Ethyl nitrate.	Insoluble.	Insoluble.	—
10. Ethyl ether (dry).	Difficultly.	Difficultly.	—
11. Acetone.	Easily.	—	Very Good.
12. Glacial acetic acid.	Slightly.	Moderately.	Good.
13. Ethyl acetate.	Moderately.	—	Good.
14. Carbon disulphide.	Insoluble.	Insoluble.	—
15. Benzol.	"	"	—
16. Nitrobenzol.	"	Difficultly.	Poor.

On heating the 3 nitro-o-phthalic acid rapidly, it begins to lose water at 207° and melts at 217° . If the determination is carried on slowly, a lower melting point is obtained. In a closed melting point tube the acid melts at 222° .

SALTS OF THE ACID.

Incidental to the work upon this acid, the writer has prepared the potassium, sodium, acid and neutral ammonium, barium and silver salts of 3 nitro-o-phthalic acid. No analytical determinations were made as all of these salts had already been carefully studied by previous investigators.

Besides these the writer attempted to make the neutral and acid aniline and toluidine salts of the acid.

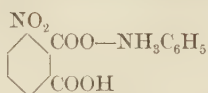
For the neutral aniline salt, 6 gms. of 3 nitro-o-phthalic acid was heated with an excess of aniline on the water bath. The acid dissolved completely and soon a crystalline precipitate formed. The mixture was distilled with steam to remove the excess of aniline and the aqueous solution remaining in the flask deposited on cooling, white needles, melting at $185\text{--}188^{\circ}$. Yield 5 gms. The salt was soluble in water and alcohol. It reacted acid to litmus, and dissolved with effervescence in sodium carbonate solution.

On being melted, water was evolved and the salt was converted to 3 nitro-phthalanil of Graebe and Buenzod.¹ No aniline was given off during the fusion.

¹ Ber. d. Chem. Ges., 32, 1992.

For the acid aniline salt, one molecule or 2.15 gms. of aniline was added to a solution of 5 gms. of 3 nitro-o-phthalic acid in alcohol. On concentration, this solution deposited white needles melting at 185° – 187° with decomposition. This salt was identical with the salt obtained when an excess of aniline was used, and also gave the 3 nitrophthalanil when fused, water being given off. The 3 nitro-o-phthalic acid therefore forms but one salt with aniline, namely, the acid aniline salt. This conclusion agrees with that found by Graëbe and Buenzod.

The salt probably has the following constitutional formula

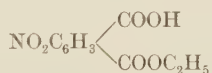


Acid-o-toluidine salt,

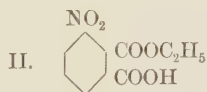
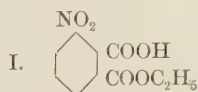


An excess of orthotoluidine was added to an alcoholic solution of the 3 nitro acid. The solution after being concentrated on the water bath deposited fine white needles melting at 181° . The salt dissolved in soda solution with effervescence and its solutions reacted acid toward litmus paper. When heated several degrees above its melting point, water was given off and it was converted to 3 nitro phthal-o-tolil (see page 22).

Acid ethyl ester of 3 nitro-o-phthalic acid,



The neutral ethyl ester of 3 nitro-o-phthalic acid melting at 45° and the acid ethyl ester melting at 110.5° , were obtained by Miller,¹ by passing dry hydrochloric acid gas into a solution of the acid in absolute alcohol. There are the following two acid ethyl esters possible :



¹ Ann. Chemie (Leibig), 208, 243.

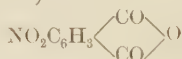
It follows from Meyer's rule that the compound obtained by Miller has the structure I. The writer in the following way has succeeded in obtaining the isomeric acid ethyl ester having the structure II.

5 gms. of 3 nitrophthalic anhydride was dissolved in 75 cc. absolute alcohol, in a flask with a reflux condenser and the solution heated for 5 hours on the water-bath. After distilling off the alcohol, a thick yellow oil remained. This oil was dissolved in a strong soda solution, and the solution extracted with ether to remove any neutral ester that might have formed (none however was obtained). The soda solution when acidified with hydrochloric acid, deposited an almost white crystalline precipitate. This compound melted at 157°.

The substance was soluble in alcohol and ether but insoluble in cold water. It reacted acid towards litmus paper and effervesced with soda solution.

.807 gm. of the substance was dissolved in alcohol and titrated with n/10 caustic soda solution using phenolphthalein as indicator. It required 33.3 cc. of the standard solution, while the theory for the acid ethyl (2) ester of 3 nitro-o-phthalic acid requires 33.76 cc. of the n/10 sodium hydrate solution.

3 nitrophthalic anhydride,



The earlier investigators state that by fusing the 3 nitro-o-phthalic acid, the anhydride was obtained. Leupold¹ found that it was difficult to obtain the pure anhydride by fusing the acid, so he heated the acid with one molecule of acetyl chloride in a sealed tube at 100°. Wegscheider and Lipschitz² boiled the acid with acetyl chloride and thus obtained the anhydride.

The writer found that the acid, after being heated for 2 hrs. at 225°, formed, on cooling, a yellowish crystalline solid, which crystallized from glacial acetic acid in needles, melting at 160–180°. This showed that the anhydride still contained some unchanged acid. If the product obtained by fusion was first dissolved and crystallized from acetyl chloride and then recrystallized from glacial acetic

¹ Dissertation. Basle, 1897, p. 20.

² Monatsch. f. Chem., 21, 787.

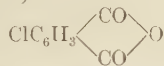
acid, needles melting at 162–163° were obtained. The melting point of 3 nitrophthalic anhydride being given by Graeff¹ as 163–164°.

The following method was found more convenient for obtaining the anhydride. The acid contained in a flask, was heated in an oil bath at 235–240°, until no trace of water could be detected by holding a watch glass over the mouth of the flask. This required 6–8 hours. On cooling, the melt formed a yellowish crystalline solid which was practically pure anhydride and could be powdered and used as such, or else crystallized from glacial acetic acid or acetone. From the latter solvent it crystallizes in white needles melting at 163°.

The 3 nitrophthalic anhydride is easily soluble in acetyl chloride, and in hot glacial acetic acid, moderately soluble in acetone or in hot alcohol, but almost insoluble in benzol.

CONDENSATIONS WITH NITROPHTHALIC ANHYDRIDE.

3 chlorphthalic anhydride,



By treating 3 nitrophthalic anhydride with phosphorous pentachloride; the writer obtained 3 chlorphthalic anhydride, instead of the 3 nitrophthalyl chloride, as was expected.

Ten gms. of 3 nitrophthalic anhydride was heated with 11 gms. (slightly more than one molecule) of phosphorous pentachloride in a sealed tube at 175° for 6 hours. On opening the tube there was considerable pressure. The contents consisted of pale yellow needles in a red fluid. The crystals were separated and recrystallized from a mixture of benzol and naphtha, forming needles melting at 122°.

This substance when heated with copper oxide gave the Beilstein test for chlorine, but when fused with sodium gave no test for nitrogen. Since by boiling with dilute acids no test for hydrochloric acid could be obtained, and the halogen was still present in the compound, it must be united to the benzol nucleus and not to the side chain.

¹ Ber. d. Chem. Ges., 15, 1127.

The compound on being boiled several hours with dilute hydrochloric acid was converted into an acid, which crystallized from water into colorless needles melting at 186° .

On analysis .1763 gm. substance by the Carius method gave .1415 gm. of silver chloride.

Found.....19.84 per cent. of chlorine.

Theory for 3 chlorphthalic anhydride, 19.44 " " " "

This substance proved to be identical with the 3 chlorphthalic anhydride made by Krüger,¹ which melts at 122° , and the corresponding acid melts at 184° .

To form this compound the phosphorous pentachloride must have replaced the nitro group by halogen according to the following reaction :



3 Chlorphthalimide.

Dissolved some 3 chlorphthalic anhydride in strong ammonia and evaporated the solution to dryness. The residue when heated gave a sublimate of white needle crystals. This substance sublimed before the melting point was reached, but melted in a closed tube at about $118-120^{\circ}$. This compound is probably 3 chlorphthalimide, which as far as can be ascertained is a new compound.

To make a nitro benzoyl benzoic acid, a mixture of the 3 nitrophthalic anhydride and dry benzol was heated on the water bath and the required amount of aluminium chloride was added gradually, in small portions. No reaction took place, as the anhydride was practically insoluble in benzol.

The method of Haller and Guyot² for making dialkylamido benzoyl-benzoic acids was next tried. To a mixture of 10 gms. of 3 nitrophthalic anhydride, 20 gms. of dimethyl aniline and 80 gms. of carbon disulphide, 20 gms. of aluminium chloride was gradually added. After the completion of the reaction the upper layer, consisting of carbon disulphide holding the excess of dimethyl aniline in solution, was decanted. The black residue was dissolved in dilute acid and the filtered solution extracted with ether.

¹ Ber. d. Chem. Ges., 18, 1759.

² Bull. Soc. Chimique [3], 25-26, 200.

The ether extract crystallized from water in hard, yellow glassy crystals, melting at 204–205°. In solubility and in other respects it behaved like 3 nitro-o-phthalic acid.

On analysis .197 gm. of substance gave 12.5 cc. of nitrogen at 22° and 750 mm. of pressure.

Found..... 7.09 per cent. of nitrogen.

Theory for 3 nitro-o-phthalic acid., 6.64 “ “

The presence of the nitro group in the anhydride probably prevented the condensation.

IMIDO DERIVATIVES OF 3 NITRO-O-PHTHALIC ACID.

The following methods were used by the writer to obtain these compounds.

1. Condensation of the nitrophthalic anhydride with a primary amine according to the following equation :



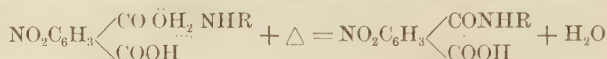
The finely powdered anhydride was thoroughly mixed with one molecule of a primary amine. The mixture contained in a large test-tube was heated in a sulphuric acid bath, into which a thermometer was inserted. The temperature of the bath was gradually raised until the reaction began, as shown by the evolution of water vapor. The heating was continued until the contents of the tube formed a quiet fusion and no more water was given off. On cooling, the melt generally formed a crystalline solid, which was then crystallized from a suitable solvent.

This method generally gave impure products because an intimate mixture of the bulky anhydride with such small amounts of primary amine could not be obtained. This fact rendered the method useless, in cases where the mixture of amine and anhydride did not melt below 250°.

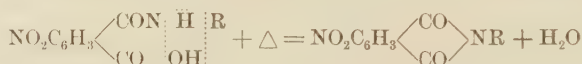
2. The second method was more satisfactory, in that an intimate mixture was obtained and therefore the resulting product was purer. Whereas in the first method the nitrophthalic anhydride, which can only be obtained from the acid with some difficulty and considerable loss, was used, this method employs the acid directly.

The imido compound was obtained by fusion of an acid salt ac-

according to the following reaction, which may take place in 2 stages.



The amic acid not being stable at the temperature employed, immediately splits up into the imide and water as follows :

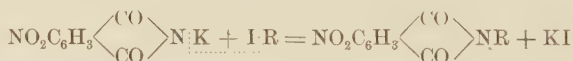


No attempt was made to isolate the intermediate product, but the writer has obtained the amic acids through a special method applied to the resulting imido compound.

The method is as follows : One molecule of a primary amine was added to an aqueous or alcoholic solution of the nitrophthalic acid. The solution on concentration generally deposited crystals of the acid-amine salt. The salt contained in a test tube was heated as in the first method. The heating was continued until the contents of the tube was in quiet fusion and no more water was evolved.

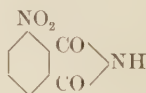
On cooling, the melt generally formed a crystalline solid consisting of the almost pure imido compound ; which could then be further purified by crystallization.

3. The reaction of the third method proceeds as follows :



A mixture of the potassium salt of nitro-phthalimide and about 1.5 molecules of an alkyl iodide, was heated in a sealed tube at 160° for two hours. The contents of the tube was washed out with cold water and the residue consisting of the impure imido compound was purified by crystallization. The results with this method were unsatisfactory, owing to the fact that the high temperature required for the reaction decomposes some of the alkyl iodide, and also to the difficulty in obtaining the pure potassium salt of the nitro-phthalimide.

3 *nitro-phthalimide*,



Laurent¹ by distilling the ammonium salt of 3 nitro-o-phthalic acid, states that the acid, instead of the expected imide was formed. He further states that by treating the anhydride with ammonia gas, a new compound was formed, but no further particulars are given.

The imide was prepared by the writer in the following way : An excess of ammonium hydrate was added to an aqueous solution of 5 gms. of 3 nitro-o-phthalic acid, and the excess of ammonia expelled by boiling the solution. To the neutral solution was then added an aqueous solution of 5 gms. of the acid and the solution concentrated. On cooling, needles of the acid ammonium salt were deposited.

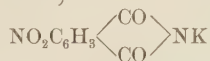
The salt contained in a test-tube was heated as described in the general method (page 15). At 225° decomposition began, and the mixture was further heated until a quiet fusion resulted and no more water was given off. On cooling, a yellowish crystalline solid was obtained. This substance was found to be easily soluble in acetone and moderately soluble in hot alcohol or glacial acetic acid and only very sparingly soluble in water. Crystallized from alcohol in pale yellow lustrous needles melting at 215-216°. Yield 8 gms. On analysis.

I. .1513 gm. substance gave 20 cc. of nitrogen at 22° and 753 mm. pressure.

II. .1694 gm. substance gave 22.1 cc. of nitrogen at 22° and 751.5 mm. pressure.

I. Found.....	14.82	per cent. of N.
II. " 	14.51	" " " "
Theory for 3 nitrophthalimide.....	14.62	" " " "

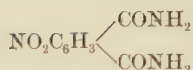
Potassium salt of the imide,



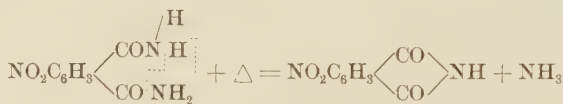
When one molecule of potassium hydrate dissolved in alcohol, was added to a weighed amount of the imide dissolved in alcohol and acetone, a white crystalline precipitate of the potassium salt forms. Heated with an excess of caustic alkali the imide decomposes with the evolution of ammonia gas.

¹ Ann. Chemie (Liebig), 41, 113.

3 nitrophthalamide,



Ammonium hydrate (.9 sp. gr.) was added to some 3 nitrophthimide contained in a beaker and the mixture warmed slightly. The lustrous flaky crystals of the imide gradually disappeared and a heavy white crystalline sandy powder formed in its place. After the mixture had been allowed to stand at ordinary temperature for one hour, the reaction was complete and the precipitate was then filtered off. The substance was dried to constant weight in a vacuum desiccator over sulphuric acid. It melted at 200–201° with evolution of ammonia gas, as shown by holding a piece of moistened red litmus paper over the mouth of the melting point tube. The substance after being once melted, remelted at 215° or the melting point of 3 nitrophthalamide, the reaction being as follows :



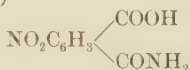
On analysis .1452 gm. substance gave 26.1 cc. of nitrogen at 22° and 758 mm. of pressure.

Found.....20.3 per cent. of N.

Theory for 3 nitrophthalamide.....20.1 “ “

The compound is therefore the 3 nitrophthalamide.

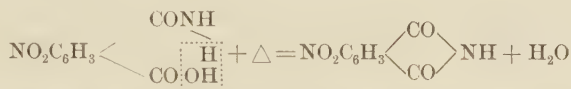
3 nitrophthalamic acid,



This acid was not obtained by treating the 3 nitrophthalic anhydride with strong ammonia or by cold digestion of the imide with 20 per cent. potassium hydrate solution, but it was, however, made by the following method : 4 gms. of 3 nitrophthalamide was added to a solution of 4 gms. of barium hydrate in 150 cc. of water. After heating for one hour at 80°, the mixture was allowed to stand 24 hours at ordinary temperature and then acidified with sulphuric acid. The barium sulphate precipitate (containing some organic matter) was filtered out and extracted with cold strong

alcohol. The alcoholic extract was concentrated by passing a current of air through it, and soon white needles were deposited. These were filtered out, washed with ether and dried in vacuo over sulphuric acid. The substance melted at 156° with evolution of water. After solidifying in the melting-point tube, it remelted at 213° , nearly the melting point of the imide, which is 215° . Yield, 1 gm.

The reaction proceeds as follows :



The filtrate from the barium sulphate precipitate on being concentrated by the same means, also deposited needles melting at 156° . Yield, .8 gm.

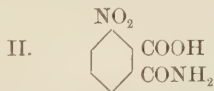
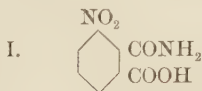
This substance which is an acid, dissolved in soda solution with effervescence, and its solutions are acid to litmus. The compound was found to be somewhat soluble in cold water, easily soluble in cold alcohol and insoluble in ether.

On analysis .1509 gm. substance gave 17.6 cc. of nitrogen at 22° and 755 mm. pressure.

Found.....13.13 per cent. of N.

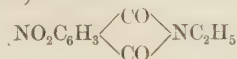
Theory for 3 nitrophthalamic acid.....13.3 " " " "

This acid may have either of the two following structures :



From the analogy between the opening up of the imide structure with a weak base, to the breaking open of the anhydride structure by means of alcohol (see page 12), in which the radical goes to the more strongly acid carboxyl and also from the slight acidity of the higher acids of this series, the writer believes that structure I. should be assigned to this compound.

3 nitroethylphthalimide,



1. A sealed tube containing 3.4 gms. of potassium 3 nitro-

phthalimide and 7 gms. of ethyl iodide was heated at 150 to 160° for 2 hours. There was considerable pressure on opening the tube, the contents being carbonized and free iodine present. No result was obtained from this tube.

2. A tube containing 4.75 gms. of potassium 3 nitrophthalimide and 5.7 gms. ethyl iodide was heated for three hours at 115° and one hour at 145°. On opening there was slight pressure and the contents was solid. This was dissolved in hot water and boiled to remove excess of ethyl iodide. On cooling the solution deposited needles which proved to be unchanged potassium salt of the imide, no other substance could be isolated.

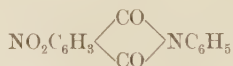
3. Since the above method failed to give any results, the following method was tried: Ethylamine gas was passed into an aqueous solution of 3 nitro-o-phthalic acid until the solution was strongly alkaline. The solution was boiled to expel the excess of ethylamine. A solution of an equal amount of the acid in water, was then added to the neutral solution thus obtained. The mixture was boiled to dryness. The residue was placed in a test-tube and fused. The reaction began at 125° and required a temperature of 165° to complete it. A greenish crystalline solid was obtained which dissolved sparingly in hot water and readily in hot alcohol.

Crystallized from alcohol in long yellowish lustrous needles melting at 105°. Yield 80 per cent. of theory. On analysis .1747 gm. substance gave 20.4 cc. of nitrogen at 27°.5 and 760 mm. of pressure.

Found.....12.85 per cent. of N.

Theory for 3 nitroethylphthalimide.....12.7 " " "

3 nitrophthalanil,

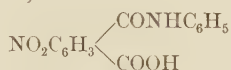


1. A mixture of 4 gms. of 3 nitrophthalic anhydride and 2 gms. (a little more than one molecule) of aniline was heated, the temperature being gradually raised to 190° and heated until the reaction was completed. Obtained an amber-like mass which was soluble in acetone, but only moderately soluble in hot alcohol. After repeated recrystallizations from a mixture of these solvents, yellow needles (free from tar) melting at 132–133°, were obtained.

2. A much better method for obtaining the 3 nitrophthalanil is the following: The acid aniline salt, obtained as previously described (page 11) was fused; a temperature of 190° was required to complete the reaction. A product similar to the above was obtained. But, as no tar was present, one crystallization of this substance from alcohol and acetone was sufficient to obtain it in the pure state. It crystallized in yellowish curved needles melting at $136-137^{\circ}$.

Graebe and Buenzod¹ heated the 3 nitro-o-phthalic acid aniline salt for 15 hours at $120-130^{\circ}$ and obtained the 3 nitrophthalanil melting at 134° .

3 nitrophthalanilic acid,



1.3 gms. of 3 nitrophthalanil was heated with a solution of 2.5 gms. barium hydrate in 150 cc. of water, at 90° for 30 minutes and then allowed to stand for 24 hours at room temperature. The reaction mixture, when acidified with dilute sulphuric acid, deposited a precipitate that was too flocculent to have consisted entirely of barium sulphate. Accordingly the precipitate was extracted with strong alcohol and the extract after being concentrated by drawing a current of air through the solution, deposited pale yellow needles, which were separated and washed with ether. The substance melted at 180° with evolution of water and after the melt had solidified, remelted at 135° , nearly the melting point of the anil.

The compound was easily soluble in alcohol, almost insoluble in cold water and in ether.

The acid does not effervesce with soda solution, but its solutions are acid to litmus paper.

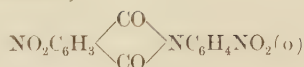
On analysis .1962 gm. substance gave 17.4 cc. of nitrogen at 23° and 758 mm. of pressure.

Found9.96 per cent. of N.

Theory for 3 nitrophthalanilic acid.....9.8 " " " "

The compound is therefore 3 nitrophthalanilic acid.

¹ Ber. d. Chem. Ges., 32, 1992.

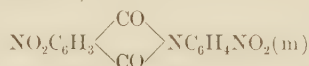
3 nitrophthal-o-nitranyl,

One molecule or 2 gms. of orthonitraniline was added to an alcoholic solution of 3.56 gms. of 3 nitro-o-phthalic acid and the mixture evaporated to dryness. The residue was heated, decomposition began at 150° and a temperature of 200° was required to complete the reaction. An amber-like solid was obtained, which crystallized from a mixture of acetone and a little alcohol, in yellow crystals melting at 167°. Yield 2.5 gms.

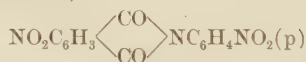
On analysis .1619 gm. substance gave 20 cc. of nitrogen at 25° and 759 mm. of pressure.

Found.....13.7 per cent. of N.

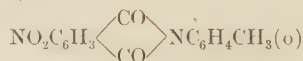
Theory for 3 nitro-phthal-o-nitranyl.....13.4 " " " "

3 nitrophthal-m-nitranyl,

Treated 2 gms. of metanitraniline in the same way. The reaction taking place between 170 and 200°. The product was less soluble in alcohol and in acetone than the compound described above. It crystallized from a mixture of these solvents, in pale brown microscopic crystals melting at 219°. Yield 2.7 gms.

3 nitrophthal-p-nitranyl,

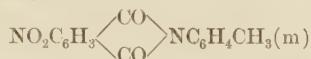
The same amounts of acid and paranitraniline were brought together, as above, and fused. To complete the reaction which began at 200°; the mixture was heated at 250°. A brown crystalline solid was obtained which was only moderately soluble in acetone, and from which solution it separated in small yellowish crystals melting at 249°.

3 nitrophthal-o-tolil,

One molecule or 1.5 gms. of orthotoluidine and 3 gms. of 3 nitro-o-phthalic acid were brought together in alcohol and the re-

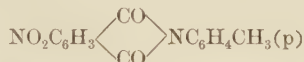
sulting solution evaporated to dryness. The residue was heated. At 160° the reaction began and was completed at 190° (at which temperature a quiet fusion was obtained). The melt, on cooling, formed an amber-like mass which was found to be easily soluble in acetone and sparingly soluble in alcohol. Crystallized from a mixture of these solvents in pale yellow needles melting at 145°. Yield 2.6 gms.

3 nitrophthal-m-tolil,



The same weights of the acid and metatoluidine were brought together as above and fused. The reaction was carried out between 160°–190°. A product similar to the above was obtained, which crystallized from a mixture of alcohol and acetone in long yellow needles melting at 129°. Yield 2.5 gms.

3 nitrophthal-p-tolil,



A mixture of 4.08 gms. of 3 nitrophthalic anhydride and one molecule or 2.25 gms. of paratoluidine was heated. At 170° the mixture melted and water was evolved, the temperature was finally raised to 180° to complete the reaction. After cooling the fusion solidified to a pale yellow crystalline solid, which when crystallized from a mixture of alcohol and acetone, formed pale yellow needles melting at 154°. Yield 5 gms.

On analysis .2003 gm. substance gave 18.3 of nitrogen at 23° and 752 mm. of pressure.

Found10.17 per cent. of N.

Theory for 3 nitro-phthal-p-tolil 9.93 “ “ “ “

3 nitro-phthalhydrazide, C₈H₅O₄N₃.

To 10 gms. of 3 nitro-o-phthalic acid dissolved in water, was added 5 gms. (a little more than one molecule) of a 50-per-cent. solution of hydrazine hydrate. The mixture was evaporated to dryness and the residue heated on an oil bath. At 150°, water was given off and the reaction was completed at 250°. The reaction product did not melt even at that temperature, but formed a

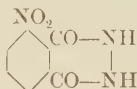
brownish porous solid. This substance was almost insoluble in water and alcohol, and was sparingly soluble in hot glacial acetic acid. It dissolved readily in hot soda solution, with evolution of carbon dioxide, forming a yellowish red solution. On acidifying this solution with hydrochloric acid the substance was thrown down as a yellowish powder. This powder crystallized from glacial acetic acid in pale yellow microscopic crystals, melting at about 320° with decomposition. Yield very good.

On analysis .151 gm. substance gave 27.4 cc. of nitrogen at 24° and 761 mm. of pressure.

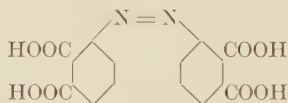
Found 20.36 per cent. of N.

Theory for $C_8H_5O_4N_3$ 20.3 " " " "

The compound behaves in most respects like phthalhydrazide of Curtius and Försterling,¹ except that it is decomposed by solutions of caustic alkali, owing to the nitro group which it contains. From the analyses and general reactions, the writer suggests the following, as the most probable structure for this substance.



Azobenzol 2,3—2,3 tetra carboxylic acid or azophthalic acid.



This compound was first made by Claus and May.² The method they employed modified in some important particulars (as given on page 39) was used by the writer to prepare the acid. The compound crystallized from hot water in golden yellow-needles, melting at 233 to 251° , and agreed in all respects with the compound of Claus and May.

AN ATTEMPT TO MAKE A NITROANTHRANILIC ACID.

In order to convert 3 nitro-phthalimide into a nitroanthranilic acid, some was dissolved in a 10-per-cent. caustic soda solution and a solution of one molecule of bromine in 10-per-cent. sodium hydrate solution was added. Carbon dioxide was evolved. The

¹ Jour. pr. Chemie [2], 51, 376.

² Ber. d. Chem. Ges., 14, 1337.

solution after being heated for 15 minutes at 75 to 85°, was nearly neutralized with hydrochloric acid, and then acidified with acetic acid. This solution gave no precipitate with cupric acetate. Nothing definite could be obtained even after evaporating the solution to dryness and extracting the residue with different solvents.

III. EXPERIMENTAL PART FOR 4 NITRO-ORTHO-PHTHALIC ACID.

PREPARATIONS OF THE ACID.

The writer used the following methods for obtaining this acid :

1. The method of Miller,¹ of which the following is a brief outline. Both the 3 and 4 nitro-o-phthalic acids are formed in the nitration of phthalic acid. By crystallizing the reaction product from water, most of the 3 nitro acid is separated. The mother liquor is evaporated to dryness and the residue dissolved in absolute alcohol, is treated for several hours with hydrochloric acid gas. On the addition of water, an oil, consisting principally of the neutral ethyl ester of 4 nitro-o-phthalic acid and some acid ethyl ester of 3 nitro-o-phthalic acid separates.

The latter is removed by washing the oil with a saturated solution of sodium carbonate. The oil then solidifies and is crystallized first from ether and then from alcohol, forming large pale yellow prisms of the neutral ethyl ester of 4 nitro-o-phthalic acid, melting at 34–35°. The ester is then decomposed by the required amount of alcoholic potash, and the precipitated potassium salt dissolved in water. The solution thus formed is acidified and extracted with ether. On evaporation of the ether, the 4 nitro-o-phthalic acid melting at 162° remains.

Although a fair yield of the acid can be obtained by this method, the ester is so difficult to purify that the resulting product is very apt to contain traces of the isomeric acid.

2. The next method tried was that published by Hoenig.² Paranitro-phthalide is heated with dilute nitric acid at 140° for four hours in a sealed tube. The contents of the tube is partly neutral-

¹ Ann. Chemie (Liebig), 208, 227.

² Ber. d. Chem. Ges., 18, 3448.

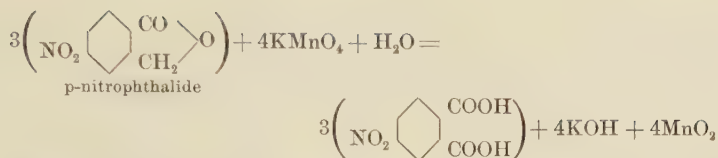
ized with alkali and extracted with ether. The ether on evaporation leaves the pure 4 nitro-o-phthalic acid. By this method, the writer was unable to obtain any of the pure acid. Possibly the nitric acid employed was not of the proper strength. Besides only small amounts of nitro-phthalide can be oxidized at one time, by employing a method requiring the use of sealed tubes.

3. Hoenig¹ states that the attempts, to oxidize para-nitro-phthalide with alkaline permanganate or with chromic acid mixture to nitro-phthalic acid, were unsuccessful. This statement is rather difficult to comprehend; as the writer has found that para-nitro-phthalide can be readily and completely oxidized to 4 nitro-o-phthalic acid, by means of alkaline permanganate. The writer has worked out the following method based on this fact, by which large amounts of the acid absolutely free from the isomeric acid can be obtained.

20 gms. of para-nitro-phthalide was dissolved in a solution of 12 gms. of sodium hydroxide in one liter of water. The solution contained in a large porcelain dish was heated on the water-bath and gradually treated with a solution of 27 gms. of potassium permanganate, until after boiling 30 minutes, the red color of the permanganate (or green color of the manganate) no longer disappears. Then a little alcohol was added to decompose the excess of permanganate, and the voluminous precipitate of manganese dioxide was best removed by using a large funnel fitted with a pleated filter paper. The precipitate was washed with hot water, and the combined filtrate and washings was acidified with hydrochloric acid and concentrated to about 150 cc. On cooling, the solution was extracted successively with 4 portions of ether of about 50 cc. each. The ether extract was dried by the addition of calcium chloride and filtered. The ether on being distilled, leaves the pure 4 nitro-o-phthalic acid as a pale yellow crystalline solid melting at 163°. The yield was about 21.8 gms. or 88 per cent. of the theory.

The amount of potassium permanganate used up, was found to be slightly more than that required, if the following reaction takes place.

¹ Ber. d. Chem. Ges. 18, 3447.



Thus 13 gms. of p-nitrophthalide reduced 16.4 gms. of potassium permanganate, instead of 15.3 gms. required by the above equation.

PROPERTIES OF 4 NITRO-O-PHTHALIC ACID.

This acid behaves in most respects like its isomer 3 nitro-o-phthalic acid. Owing to its great solubility in nearly all of the ordinary solvents, it cannot readily be crystallized. The acid obtained through Miller's method melts at 162° , while that obtained from p-nitro-phthalide melts at 163° . When heated slightly above its melting point, it loses water and is partly converted into anhydride.

SOLUBILITY OF 4 NITRO-O-PHTHALIC ACID.

Solvent.	Cold.	Hot.	Crystals on Cooling.
1. Water.	Easily.	Very easily.	Poor.
2. Petroleum ether.	Insoluble.	Insoluble.	_____
3. Benzine.	"	"	_____
4. Chloroform.	"	"	_____
5. Carbon tetrachloride.	"	"	_____
6. Methyl alcohol.	Easily.	_____	_____
7. Ethyl alcohol (absol.).	"	_____	_____
8. Isoamyl alcohol.	Sparingly.	Easily.	Fair.
9. Ethyl nitrate.	Insoluble.	Insoluble.	_____
10. Ethyl ether (dry).	Moderately.	Moderately.	_____
11. Acetone.	Easily.	_____	Fair.
12. Glacial acetic acid.	Sparingly.	Easily.	Good.
13. Ethyl acetate.	Moderately.	_____	_____
14. Carbon disulphide.	Insoluble.	Insoluble.	_____
15. Benzol.	"	"	_____
16. Nitrobenzol.	"	Moderately.	Fair.

SALTS OF THE ACID.

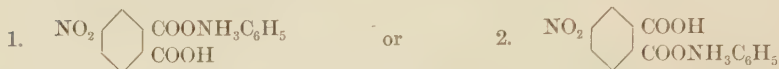
The writer has made the potassium, acid and neutral ammonium and silver salts of 4 nitro-o-phthalic acid, all of which have been previously prepared by Miller.¹

Attempts similar to that described on pages 10-11 were made to prepare both the neutral and acid aniline salts of this acid.

¹ Ann. Chemie (Liebig), 208, 223.

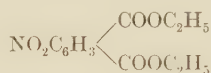
Only the acid aniline salt melting at 181 to 182° was obtained. This result agrees with that found by Gräbe and Buenzod.¹

This salt may have either of the following formulas.



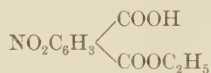
If the conclusion arrived at on page 6 be true, that the carboxyl para to the nitro group is the more strongly acid carboxyl, then structure 2 would be correct for this salt. But this conclusion is not based on very strong proof. In fact the acid acts in some cases as if both carboxyl groups were of equal strength.

Ethyl ester of 4 nitro-o-phthalic acid,



This was obtained as described on page 25.

Acid ethyl ester of 4 nitro-o-phthalic acid,



Miller² states that by evaporating an alcoholic solution of 4 nitrophthalic anhydride, an acid ester forms, which appears to be different from the ordinary acid ester.

The writer accordingly dissolved 3 gms. of the anhydride in 50 cc. of absolute alcohol, and boiled the solution contained in a flask with a reflux condenser, for 8 hours on the water bath. The alcohol was then distilled, leaving a reddish-brown oil, which dissolved readily in an aqueous sodium carbonate solution with evolution of carbon dioxide. The solution was first extracted with ether, in order to remove any neutral ester that might have formed, and then acidified with hydrochloric acid. The turbid acid solution was then extracted with ether. The ethereal solution was dried with calcium chloride, filtered and the ether distilled. A yellow oil remained, which solidified to a pale yellow amorphous mass after standing about eight hours in vacuo over sulphuric acid. This substance melted at 141–150°. Yield 2.6 gms. After

¹ Ber. d. Chem. Ges., 32, 1993.

² Ann. Chemie (Liebig), 208, 235.

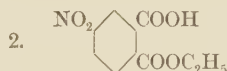
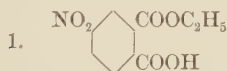
crystallizing the compound from dilute alcohol, it gave the same melting point.

The ordinary acid ester of 4 nitro-o-phthalic acid, melting at 127–128°, was prepared by Miller, by treating a solution of the acid in absolute alcohol, for a short time with hydrochloric acid gas.

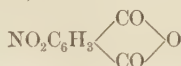
From the method used for the preparation of this compound, and from the fact that its melting point, although not sharp, was considerably higher than for the ordinary acid ester, it follows that this substance is an isomeric acid ethyl ester of 4 nitro-o-phthalic acid, or else the substance consists of a mixture of the isomer with the ordinary acid ethyl ester.

This result is opposed to that obtained by Wegshieder and Lipschitz.¹ They claim that the same acid methyl ester of the acid was obtained, either by treating the acid with methyl alcohol and hydrochloric acid or by boiling the anhydride with methyl alcohol.

Which of the following two formulas can be assigned to the ordinary acid ethyl ester of 4 nitro-o-phthalic acid or which to the isomeric ester acid is not known.



4 nitrophthalic anhydride,



By heating 4 nitro-o-phthalic acid at 165° until no more water was given off, a yellowish sticky mass was formed, after the fusion had cooled. Miller heated this sticky substance to 200° and sublimed the anhydride by passing a current of air through the fused mass. Instead of subliming the anhydride, which was difficult and caused considerable loss, the writer treated the sticky substance obtained by fusion, with acetyl chloride. The solution thus obtained was evaporated to crystallization. Pale yellow crystals of the anhydride, melting at 114°, were obtained. The anhydride was easily soluble in acetyl chloride, in hot glacial acetic acid and in hot alcohol. It was sparingly soluble in benzol and insoluble in cold water.

¹ Monats. f. Chemie (Wien.), 21, 787.

CONDENSATIONS WITH 4 NITRO-PHTHALIC ANHYDRIDE.

The following attempts to prepare 4 nitro-phthalylchloride were unsuccessful.

1. Heated 5 gms. of the anhydride with a little more than one molecule of phosphorous pentachloride in a sealed tube for 5 hours at 160° . On opening the tube there was considerable pressure and the contents was liquid. The reaction mixture was heated at 200° until all the phosphorous compounds had distilled. A yellowish residue, which was partly soluble in benzol, remained. This gave no definite compound on crystallization, and did not give the reactions of an acid chloride.

2. One molecule of phosphorous pentachloride and 5 gms. of the anhydride were brought together in a flask with a return condenser and heated to slow boiling on a sand-bath for 40 hours. The phosphorous compounds were then removed by heating the reaction product at 250° . The residue when crystallized from benzol gave reddish needles, melting below 100° . These gave a slight test for halogen, but no hydrochloric acid when boiled with water, and no 4 nitrophthalamide when treated with strong ammonia. This method also failed to give 4 nitro-phthalyl chloride.

3. Heated 5 gms. of the potassium salt of 4 nitro-phthalic acid with an excess of phosphorous oxychloride, in a sealed tube, for 4 hours at 140° . The contents of the tube was added to ice water; a white crystalline residue remained undissolved. This substance gave only a faint test for chlorine and melted at 115° . It proved to be 4 nitro-phthalic anhydride.

In order to form a substituted benzoyl benzoic acid; a solution of 5 gms. of 4 nitro-phthalic anhydride in 50 cc. of benzol, was heated on the water-bath, and then was added, 7.5 gms. of aluminium chloride in small portions at a time, during 3 hours. The residue remaining, after distilling the benzol, was decomposed with dilute hydrochloric acid. The portion not dissolved by the acid was only slightly soluble in sodium carbonate solution and consisted mostly of unchanged anhydride. Nothing definite resulted from this experiment.

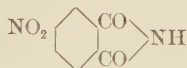
An attempt to prepare a nitro derivative of dimethyl amido

benzoyl benzoic acid by the method as given on page 14, also proved unsuccessful. A yellowish crystalline substance melting at 158–159° and having acid properties was obtained. In solubility and in other particulars, it behaved like 4 nitro-o-phthalic acid. An analysis of its silver salt gave 47.3 per cent. of silver, whereas the silver salt of 4 nitro-o-phthalic acid contains 50 per cent. of silver.

IMIDO DERIVATIVES OF 4 NITRO-O-PHTHALIC ACID.

The methods employed to prepare these compounds were the same as those used to obtain similar derivatives of 3 nitro-o-phthalic acid, as given on pages 15–16. The derivatives of the former, differ from the corresponding derivatives of the latter, in that they crystallize less readily, and in having higher melting points.

4 nitrophthalimide,



This compound had already been made by the writer 6 months previous to the time that the article published by Fränkel¹ appeared. In this article he states that he had obtained the imide from 4 nitro-o-phthalic acid, but does not mention how he prepared it. The compound crystallized from water in white needles melting at 193–195°.

The method used by the writer to prepare this compound was as follows: The acid ammonium salt of 4 nitro-o-phthalic acid was made by the usual method. The salt contained in a test-tube was heated in a sulphuric-acid bath. At 225° the salt began to decompose with evolution of water, and the heating was continued at that temperature, until no more water was given off, and a quiet fusion resulted. (This required about one hour.) On cooling, the melt formed a crystalline solid, which was found to be easily soluble in acetone and sparingly soluble in hot alcohol and hot water. Crystallized from a mixture of alcohol and acetone in pale yellowish brown flakes melting at 197°. Yield from 80–90 per cent. of the theoretical.

¹ Ber. d. Chem. Ges., 33, 2811.

ANALYSIS.

I. .1804 gm. substance gave 24 cc. of nitrogen at 23° and 755 mm. of pressure.

II. .1494 gm. substance gave 19.9 cc. of nitrogen at 22° and 756 mm. of pressure.

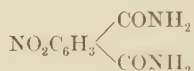
I. Found.....14.96 per cent. of N.

II. "15 " " " "

Theory for 4 nitrophthalimide.....14.62 " " " "

The potassium salt of this compound was made by adding a solution of one molecule of potassium hydroxide in alcohol, to a known amount of the imide, dissolved in a mixture of alcohol and acetone. The salt came down as a white crystalline precipitate, only slightly soluble in strong cold alcohol, but readily soluble in water.

4 nitrophthalimide,



Some 4 nitrophthalimide was added to strong ammonium hydrate (.9 sp. gr.). On warming slightly, the imide dissolved, and after standing at room temperature for one hour, the solution deposited a heavy white crystalline precipitate, which was filtered out and washed with a little cold water, and dried to constant weight in a vacuum desiccator over sulphuric acid.

The compound melted at 200° with evolution of ammonia gas, as shown by holding a strip of moist red litmus paper over the mouth of the melting-point tube. After solidifying; the substance in the tube remelted at 197°, which is the melting point of the imide.

On analysis .143 gm. substance gave 25.9 cc. of nitrogen at 22°.5 and 755 mm. of pressure.

Found.....20.3 per cent. of N.

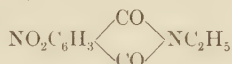
Theory for 4 nitrophthalimide.....20.1 " " " "

4 NITROPHTHALAMIC ACID.

Although many attempts to prepare this acid were made, the writer was unable to obtain the compound in a pure state. One of these attempts was as follows:

2.5 gms. of 4 nitro-phthalimide was added to a solution of 2.5 gms. of barium hydrate in 150 cc. of water. The mixture was heated for 45 minutes at 75°. Traces of ammonia gas could be detected coming off. After allowing the solution to stand 24 hours, dilute sulphuric acid was added to acid reaction. The precipitated barium sulphate was filtered off, and the filtrate concentrated by means of a current of air. A yellowish-white solid was thus obtained, which melted at 127 to 128° with carbonization. Owing to its great solubility in water or alcohol, the substance could not be freed from traces of sulphuric acid and therefore could not be obtained pure enough for an analysis.

4 nitroethyl phthalimide,



This compound was made by two different methods: (1) a mixture of 5 gms. of the dry potassium 4 nitro-phthalimide and 5 gms. (an excess) of ethyliodide was heated in a sealed tube for 2 hours at 150°. There was no pressure on opening the tube, and the contents consisted of a reddish crystalline mass. This was washed with cold water and the residue filtered off. This substance was slightly soluble in hot water, but easily soluble in alcohol or ether. Crystallized from alcohol in small leafy crystals melting at 100–104°. This substance was further purified by dissolving it in ether and washing the ethereal solution with a saturated sodium carbonate solution. The residue, after distilling off the ether, was crystallized from alcohol, forming pale yellow leafy crystals melting at 111–112°. On analysis .1805 gm. substance gave 20.6 cc. of nitrogen at 23° and 758 mm. of pressure.

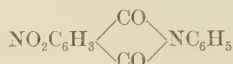
Found.....12.83 per cent. of N.

Theory for 4 nitroethyl-phthalimide12.7 “ “ “ “

2. An excess of ethylamine gas was passed into a solution of 3 gms. of 4 nitro-o-phthalic acid in water. The solution was boiled until the excess of ethylamine was driven off. Then an aqueous solution of 3 gms. of the 4 nitro acid was added, and the mixture evaporated to dryness and heated in an oil-bath. At 128° the reaction began and was completed at 160°. On cooling the fused

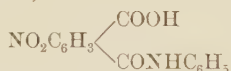
product formed a yellowish crystalline solid ; which was soluble in alcohol and sparingly soluble in hot water. Crystallized from alcohol in small crystals, melting at 111° . Yield 4.6 gms.

4 nitrophthalanil,



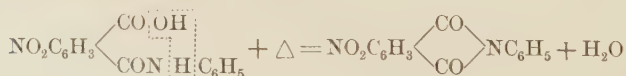
By fusing the acid aniline salt of 4 nitro-o-phthalic acid at 190° until a quiet fusion resulted and no more water was evolved, a pale brown crystalline solid was obtained, when the melt had cooled. This substance was moderately soluble in acetone and sparingly soluble in alcohol. It crystallized from a mixture of these solvents in yellow needles, melting at 194° . The 4 nitrophthalanil was first made by Graebe and Buenzod¹ by heating the acid aniline salt for 15 hours at 120 – 130° . The compound thus obtained melted at 192° .

4 nitrophthalanilic acid,



Added 1.5 gms. of 4 nitrophthalanil to a solution of 1.5 gms. of barium hydrate in 150 cc. of water. The mixture was heated for 30 minutes at 90° and after standing at room temperature for 24 hours, the solution was acidified with dilute sulphuric acid. The precipitate of impure barium sulphate thus obtained was filtered out. The filtrate when evaporated to dryness, left no residue. The precipitate was, therefore, extracted with strong alcohol, and after filtering the alcohol solution and concentrating it by means of a current of air, pale yellow crystals were obtained. These were separated, washed with water and then with ether, and dried in vacuo over sulphuric acid. The compound melted at 181° with evolution of water. After solidifying in the melting-point tube, it remelted at 193° , nearly the melting point of the anil, which is 194° .

The reaction proceeds as follows :



¹ Ber. d. Chem. Ges., 32, 1993.

The acid dissolved readily in cold alcohol; was almost insoluble in ether and in cold water.

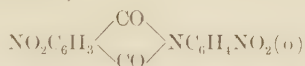
It did not effervesce with soda solution, but its alcoholic solution was strongly acid to litmus.

On analysis .1955 gm. substance gave 17.2 cc. of nitrogen at 25° and 761 mm. pressure.

Found.....9.83 per cent. of N.
Theory for 4 nitrophthalanic acid9.8 " " " "

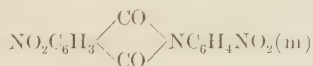
The melting-point determination, the acidity of the compound and the analysis, prove that the compound is 4 nitrophthalanic acid. The structure of this compound is as yet undetermined (see pages 6 and 29).

4 nitrophthal-o-nitranyl,

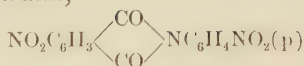


In a beaker, were brought together one molecule (or 2 gms.) of orthonitraniiline and 3.06 gms. of 4 nitro-o-phthalic acid dissolved in alcohol. The mixture was evaporated to dryness and the residue placed in a large test-tube, was fused. At 150° the reaction began and was completed at 230°. On cooling, the reaction product formed a yellowish brown crystalline solid. This substance was difficultly soluble in acetone and very slightly soluble in alcohol, but readily soluble in boiling nitrobenzol. Crystallized from the latter solvent in pale yellow needles. These were separated, washed with strong alcohol and dried at 100°. The compound melted at 233°. Yield 2.5 gms.

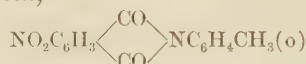
4 nitrophthal-m-nitranyl,



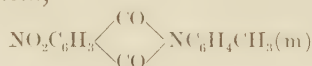
2 gms. of metanitraniiline and 3.06 gms. of 4 nitro-o-phthalic acid were brought together and treated as above. The reaction taking place between 135° and 245°. A yellowish solid was thus obtained, which was sparingly soluble in alcohol or acetone, but readily soluble in boiling nitrobenzol. The substance crystallized from the latter solvent, in bunches of opaque yellow needles melting at 243.

4 nitrophthal-p-nitranyl,

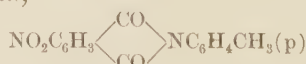
2 gms. of paranitraniline and 3.06 gms. of 4 nitro-o-phthalic acid were brought together and treated as above. The reaction began at 150° and was completed at 255°. A reddish brown solid was obtained which was difficultly soluble in acetone, insoluble in alcohol and soluble in boiling nitrobenzol. Crystallized from the latter solvent, in small yellow crystals melting at 251–253°.

4 nitro phthal-o-tolil,

To an alcoholic solution of 3 gms. of 4 nitro-o-phthalic acid was added, one molecule or 1.5 gms. of orthotoluidine. The mixture was evaporated to dryness and the residue obtained was heated. Water first began to come off at 150° and at 190° the reaction was completed. On cooling, the reaction product formed an amber-like mass which was slightly soluble in alcohol and moderately soluble in acetone. Crystallized from acetone, as a brownish crystalline powder, melting at 160°. Yield 2.4 gms.

4 nitro phthal-m-tolil,

3 gms. of 4 nitro-o-phthalic acid and 1.5 gms. of metatoluidine were brought together and treated as above. The reaction began at 175° and was completed at 200°. A yellowish crystalline mass resulted, which was found to be insoluble in alcohol, difficultly soluble in acetone and readily soluble in hot nitrobenzol. Crystallized from the latter solvent in brownish crystals, melting at 197°. Yield 1.9 gms.

4 nitrophthal-p-tolil,

A mixture of 3.48 gms. of 4 nitrophthalic anhydride and one molecule or 1.93 gms. of paratoluidine, contained in a test-tube, was heated in an oil-bath. At 180° the reaction began, and the

heating was continued at 190° until a quiet fusion was obtained and no more water was evolved. The reaction product on cooling, formed a crystalline mass, soluble in acetone and slightly soluble in alcohol. Crystallized from a mixture of these solvents in yellow lustrous flakes, melting at 165° ,

On analysis .1935 gm. substance gave 17.5 cc. of nitrogen at $22^{\circ}.5$ and 751 mm. of pressure.

Found.....10.14 per cent. of N.

Theory for 4 nitrophthal-p-tolil 9.93 " " " "

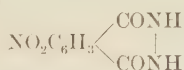
4 nitrophthal-p-tolilic acid,



To a solution of 2.5 gms. of barium hydrate in 150 cc. of water, was added 1.85 gms. of 4 nitrophthal-p-tolil. The mixture was heated 15 minutes on the water-bath. The flaky crystals of the tolil were gradually replaced by long yellow needles. After allowing the mixture to stand 24 hours, the crystals were filtered off. On ignition the substance left considerable ash, which was found to consist of barium oxide. The substance was therefore a barium salt.

To obtain the free acid, the barium salt was decomposed with dilute sulphuric acid. The precipitate consisting of barium sulphate and organic matter was filtered off. The filtrate left no residue on evaporation. The precipitate was therefore extracted with strong alcohol and the residue of barium sulphate filtered out. The alcoholic extract when evaporated by means of a stream of air, left white needle crystals which were insoluble in ether and in cold water. The substance melted at 172° with evolution of water and after solidifying in the melting-point tube, remelted at 165° , which is the melting point of 4 nitrophthal-p-tolil. The acid does not effervesce with sodium carbonate solution, but its alcoholic solution is acid to litmus.

4 nitrophthalhydrazide,



This compound was prepared by two different methods.

1. An alcoholic solution of 5 gms. of 4 nitrophthalic anhydride was heated with one molecule (or 2.5 gms. of a 50-per-cent. solution) of hydrazine hydrate. No precipitate formed, after heating the solution several hours. The solution, when evaporated to dryness on the water bath, left a thick red oil which on the addition of water deposited a yellowish brown precipitate. This precipitate was boiled down repeatedly with fresh additions of water, and was finally treated with cold water, filtered off, and washed with water, alcohol and finally ether. This substance was sparingly soluble in water or alcohol, but readily in warm soda solution, to a red solution, with evolution of carbon dioxide. On acidifying the alkaline solution, a pale yellow flocculent precipitate separated.

This substance when crystallized from water, formed a yellowish crystalline powder which did not melt even at 300° .

On analysis .1503 gm. substance gave 27.4 cc. of nitrogen at 24° and 750 mm. of pressure.

Found	20.16 per cent. of N.
Theory for 4 nitrophthalhydrazide.....	20.3 " " " "

2. One molecule of hydrazine hydrate was added to an aqueous solution of 5 gms. of 4 nitro-o-phthalic acid. The mixture was evaporated to dryness and the residue heated. At 150° , water was given off and the substance began to soften. When the evolution of water had ceased; the temperature was gradually raised to 250° , but the substance in the tube did not melt. A pale brown solid was thus obtained, which dissolved in hot soda solution, with evolution of carbon dioxide, to a red solution. A flocculent yellow precipitate separated, when this solution was acidified.

The precipitate was sparingly soluble in alcohol or water and difficultly soluble in glacial acetic acid. Crystallized from the latter solvent in small yellow crystals, which when heated gave off a white sublimate at 270° , darkened at 280° , but did not melt even at 300° .

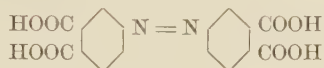
On analysis .1733 gm. substance gave 32 cc. of nitrogen at 22° and 743 mm. of pressure.

Found.....	20.45 per cent. of N.
Theory of 4 nitrophthalhydrazide.....	20.3 " " " "

By heating this compound several hours with acetic anhydride, no definite acetyl derivative was obtained. The same compound was obtained by each of the two methods employed. From the way the compound was prepared and also from its behavior, it is probable that the compound has the following formula, although this still remains to be proved.



Azobenzol 3,4-3,4 tetracarboxylic acid,



The azophthalic acid formed by the reduction of 3 nitro-o-phthalic was prepared by Claus and May¹, but they did not try to obtain the isomeric acid resulting from the reduction of 4 nitro-o-phthalic acid. This, the writer has prepared in the following way.

To 10 gms. of 4 nitro-o-phthalic acid dissolved in water and contained in a 500 cc. flask, was added enough of a 2-per-cent. solution of sodium hydrate (about 200 cc.) to render the solution alkaline. The flask was placed in a dish of cold water and then was added 280 gms. of sodium amalgam (6 gms. of sodium in 274 gms. of mercury) in small portions at a time, and with vigorous shaking after each addition. When all the amalgam had been added, the solution was heated on the water-bath for one hour. The red alkaline solution thus obtained was decanted from the mercury, concentrated, and then acidified with hydrochloric acid. A copious yellowish-red precipitate separated, which was filtered off and dried.

This substance was moderately soluble in hot water, and only slightly soluble in alcohol or glacial acetic acid, and insoluble in ether.

Crystallized from water as a salmon-pink crystalline powder which does not melt at 360°. An aqueous solution of this substance was acid to litmus, and dissolved in soda solution with effervescence.

That this compound did not contain the hydrazo union, was

¹ Ber. d. Chem. Ges., 14, 1337.

shown by the fact that it was not changed by boiling with a solution of sodium nitrite in glacial acetic acid.

On analysis .2046 gm. substance gave 14 cc. of nitrogen at 23° and 762 mm. of pressure.

Found7.73 per cent. of N.

Theory for azobenzoltetracarboxylic acid...7.8 " " " "

Silver salt of the acid, $C_{16}H_6O_8N_2Ag_4$.

This salt was made by adding a strong aqueous solution of silver nitrate, to a solution of the acid neutralized with ammonia. The red precipitate which separated, was insoluble in hot water. When dried to constant weight at 110° the salt formed a heavy red powder.

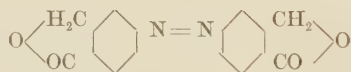
On ignition of .2039 gm. of the salt, .1085 gm. of silver remained.

Found.....53.2 per cent. of Ag.

Theory for $C_{16}H_6O_8N_2Ag_4$54.9 " " " "

The low result was probably due to the loss caused by the explosive violence with which the silver salt decomposes when heated above a certain temperature.

Azophthalide,



This substance was made by dissolving 10 gms. of paranitrophthalide in sufficient 2-per-cent. sodium hydrate solution, to render the solution slightly alkaline. To this solution was added gradually 300 gms. of an amalgam, consisting of 6 gms. of sodium in 294 gms. of mercury. The reaction was carried out, as for the preceding compound. On acidifying the red alkaline solution thus obtained with hydrochloric acid, a red precipitate formed, which was filtered off and dried. This substance was found to be sparingly soluble in hot water and moderately soluble in alcohol and glacial acetic acid. From a diluted alcoholic solution the substance crystallized in small red crystals, melting at 260–280° with decomposition. Yield, 5.8 gms.

On analysis .200 gm. substance gave 17.6 cc. of nitrogen at 26° and 756 mm. of pressure.

Found	9.6 per cent. of N.
Theory for azophthalide	9.5 " " " "

An alkaline solution of azophthalide was oxidized with potassium permanganate, using the method outlined on page 26. The filtrate, from the precipitate of manganese dioxide, when acidified with hydrochloric acid, deposited a reddish crystalline precipitate. This when separated and dried, melted at $285-300^{\circ}$ with decomposition.

On analysis .1946 gm. substance gave 13 cc. of nitrogen at 22° and 752 mm. of pressure.

Found	7.8 per cent. of N.
Theory for azo-benzol tetracarboxylic acid } expected as the result of the oxidation.. }	7.8 " " " "

The silver salt of this compound formed a heavy red powder, which was partly soluble in hot water. On ignition of .2031 gm. of the dried silver salt, obtained .1024 gm. of silver.

Found	50.4 per cent. of Ag.
Theory for $C_{16}H_6O_8N_2Ag_4$ Ag. salt azobenzoltetracarboxylic acid. }	54.9 " " " "

This salt explodes when ignited.

Although by oxidation of azophthalide an acid was obtained which contains 4 carboxyl groups (as shown by the analysis of its silver salt) and has the correct per cent. of nitrogen corresponding to azobenzol, 3, 4-3, 4 tetra carboxylic acid, yet it differs from the latter compound in melting at 300° (whereas the latter does not melt even at 360°) and in the solubility of its silver salt in hot water. Perhaps the permanganate oxidation went further than expected and an azoxyphthalic acid was produced.

ATTEMPT TO OBTAIN A NITRO-ANTHRANILIC ACID.

Dissolved 5 gms. of 4 nitrophthalimide in 50 cc. of a 20-per-cent. sodium hydrate solution. Then added a solution of one molecule of bromine dissolved in an aqueous 10-per-cent. solution of caustic soda. An evolution of carbon dioxide took place. The mixture was heated for 15 minutes at 80° and on cooling was acidified with hydrochloric acid, which caused a yellowish-red precipitate to separate. This substance was soluble in alcohol, ether

and hot water. Crystallized from water in orange-colored needles melting at 195 to 215°. The presence of the amido group in the compound was shown, by the isonitrile reaction that was obtained when the substance was heated with a mixture of alcoholic potash and chloroform, and also by the fact that it could be diazotized. The substance gave a test for halogen when heated with copper oxide. That the halogen atom was united to the benzol nucleus, and not present in the form of an acid salt, was shown by the fact that an aqueous solution of the compound gave no precipitate of silver halide with silver nitrate solution. Also the substance dissolved in soda solution with effervescence and its solutions were acid to litmus.

The presence of carboxyl, amido and halogen groups in the substance was proved. The melting point seems to indicate that the substance consists of a mixture of different compounds. The failure to obtain a definite nitro-anthranilic from 4 nitrophthalimide is, in the writer's opinion, due to the fact that in the presence of strong alkali a secondary reaction took place, in which the nitro group was partly or entirely replaced by halogen.

Where not otherwise stated, the derivatives of the nitrophthalic acids made by the writer, as described in the preceding work, are as far as could be ascertained new compounds.

IV. CONCLUSIONS.

The work by the writer upon the mono-nitrophthalic acids has shown :

1. That in nearly all cases these two isomer acids react toward reagents in the same way, giving similar products.
2. That imido, amido and amic acid derivatives similar to those derived from ortho-phthalic acid, can be obtained from these acids.
3. That alkaline solutions of the acids can be readily reduced to azophthalic acids by sodium amalgam.
4. That under certain conditions the nitro group present in these acids can be directly replaced by halogen.

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BIOGRAPHICAL.

Leopold Boroschek, graduated from the public schools of New York City, in 1892, entered the College of the City of New York and graduated from that institution in 1897, with the degree of Bachelor of Science.

In October, 1897, he entered Columbia University, receiving the degree of Master of Arts, under the Faculty of Pure Science, in June, 1900.

During 1900-1901 he pursued post-graduate studies in chemistry under the Faculty of Pure Science of Columbia University, leading to the degree of Doctor of Philosophy.



